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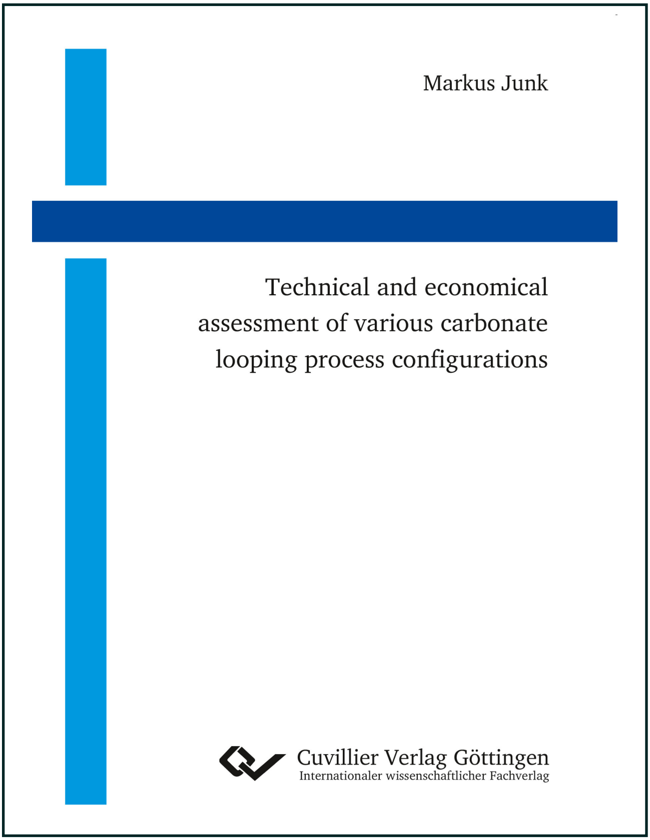

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Cuvillier Verlag Göttingen
Internationaler wissenschaftlicher Fachverlag

1 Introduction

Earth's population has risen about tenfold from 600 million people in 1700 to 6.3 billion in 2003, and by 2050, the human population will probably be again larger by 2 to 4 billion people [1]. The energy demand will consequently increase and even 2 billion people, especially in Africa, will not have any continuous access to commercial energy. Energy is critical to global prosperity, as it underpins economic growth, social development, and poverty reduction [2]. However, with more than 80 % of global energy from fossil fuel, growing energy demand has led to increasing greenhouse gas emissions. More people are seeking for more prosperity.

The worldwide energy consumption has doubled within the last 30 years. The amount of cars during this time period has even been tripled especially caused by industrialized countries. These countries only represent 20 % of the earth's population consuming more than 60 % of the energy produced. Today's challenge is to decouple economic growth and social development from increasing emissions. This requires action by central and local governments, publicly and privately owned businesses, communities and individuals [2].

1.1 Motivation

Weather recording, the evaluation of proxy data and paleo-climatic investigations as ice core spannings and tree rings provide useful information for the global climate reconstruction of several million years. It is obvious that the climate has changed especially from the beginning of the industrialization starting by the middle of the 18th century. Global atmospheric concentrations of carbon dioxide, methane and nitrous oxide have increased markedly as a result of human activities. The global increase in carbon dioxide concentration are primarily due to the changed use of fossil fuel and land, while the increase numbers of methane and nitrous oxide are primarily due to agriculture. Changes in the atmospheric abundance of greenhouse gases and aerosols, in solar radiation and in land surface properties have altered the energy balance of the climate system. These changes are expressed in terms of radiative forcing which is used to compare how a range of human and natural factors drive warming or cooling influences on global climate [3].

The radiative forcing is measured by the net radiative flux change in the atmosphere. Several quantitative definitions of radiative forcing are applied, their differences depending on the atmospheric level at which the flux change is computed. The simplest useful definition is the instantaneous flux change in the tropopause [4]. Ramaswamy et al. [5] defines it as "*the change in net (down minus up) irradiance (solar plus longwave; in W/m^2) at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values*". The strongest radiative forcing and thus the largest atmospheric driver of climate change is caused by the increased concentration of carbon dioxide (CO_2) in the atmosphere [6]. The concentration of CO_2 in the atmosphere has increased by 40 % since 1750. But there are several further greenhouse gases that have a positive radiative force, e. g. methane (CH_4), nitrous oxide (N_2O), halocarbons or ozone (O_3). The forcing value of all greenhouse gases increases due to human activities, because each gas absorbs the outgoing infrared radiation in the atmosphere. Natural forcing arises due to solar changes. Solar output has increased gradually in the industrial area, causing a small positive radiative forcing. This has come in addition to the standard solar cyclic changes. Nevertheless, the differences in radiative forcing between 2011 and the start of the industrial revolution of solar irradiance changes compared to the forcing due to human activities are very small. Therefore, the radiative forcing from human activities is much more significant for the climate change than the estimated radiative forcing from natural processes [7].

1.2 CO_2 Emissions

CO_2 is responsible for more than 76 % of the anthropogenic greenhouse gas emissions, whereof more than 86 % are caused by the combustion of fossil fuels and industrial processes and the rest by forestry and other land use [8]. When referring the energy related CO_2 emissions to different sectors around 39 % are produced by power generation. Figure 1 shows the energy related CO_2 emission separated by economic sectors, and region till 2014 [9].

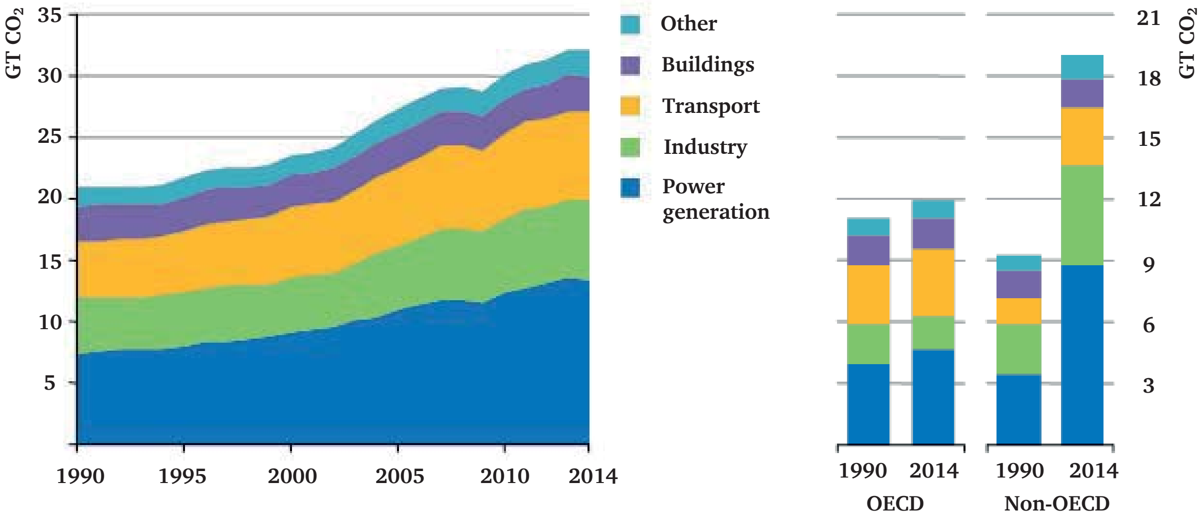

Figure 1: Global Energy related CO_2 emissions by economic sector and region (gigatonne of CO_2-equivalent per year) [9]

The average annual rate of increase of CO_2 emissions from 2000 till 2014 was 2.3 % per year, especially driven by a rapid rise of emissions from power generation in non-OECD countries. Figure 1 shows that the emissions in the power generation sector in these countries nearly tripled during the last 15 years. China is responsible for almost two third of this increase. The emissions by industries (i.e. cement or steel) in emerging and developing countries have nearly doubled, whereas the emissions from OECD countries in this sector have decreased by around one quarter. Though, the OECD countries are still responsible for the majority of the CO_2 emissions in the transport sector. This is due to the high level of ownerships of private vehicles and the strong increase in freight [9].

The majority of global CO_2 emissions are generated solely by very few countries. In 2012 more than 50 % of the total emissions were produced by China, India and the United States. China overtook the Unites States in the year 2006. Having emitted around 3 Gt of CO_2 in the year 2000 China tripled their emissions to nearly 9 Gt in the year 2014. The emissions in India are also rising. From 1990 until 2014 the emitted CO_2 nearly doubled [9]. Nevertheless, it has to be stated that the emissions per person are still higher in the OECD countries.

The global climate change is caused by human activities. If the greenhouse gas emissions are not limited in the future, it is very likely that further climate changes with severe consequences will be caused. Consequently, a 2 °C limitation objective was announced after the UN climate conference 2010 in Cancun [10]. This scenario is equivalent to a CO_2 volume faction of 450 ppm in the atmosphere. The global concentration of carbon dioxide in the atmosphere reached 400 parts per million (ppm) for the first time in recorded history in March 2015, according to data from the Mauna Loa Observatory in Hawaii [11]. Since the beginning of this record, the carbon dioxide emissions have increased by around 24 %. Figure 2 shows the characteristic for the CO_2 concentration in the atmosphere from 1958 till 2015.

If a limitation to 450 ppm of CO_2 in the atmosphere can be achieved, the damages caused by climate change will supposedly be economically and socially sustainable. To reach this objective, the global greenhouse gas emissions have to be decreased by a minimum of 50 %. This goal is faced by the worldwide rising energy demand due to the increasing world population especially in emerging and industrialized countries. The International Energy Agency (IEA) estimates an increase of the demand for electricity by 70 % from 5,429 GW in the year 2011 to 9,340 in the year 2035 [2]. China and India alone will be responsible for about 50 %. Coal will continue to be an important fossil fuel for the worldwide electricity production. Despite the fact that energy production from renewable resources will more and more be deployed in different countries, the IEA assumes that the absolute amount of burnt coal will even increase until 2035. Thus, the emission of CO_2 is strongly dependent on government decisions.

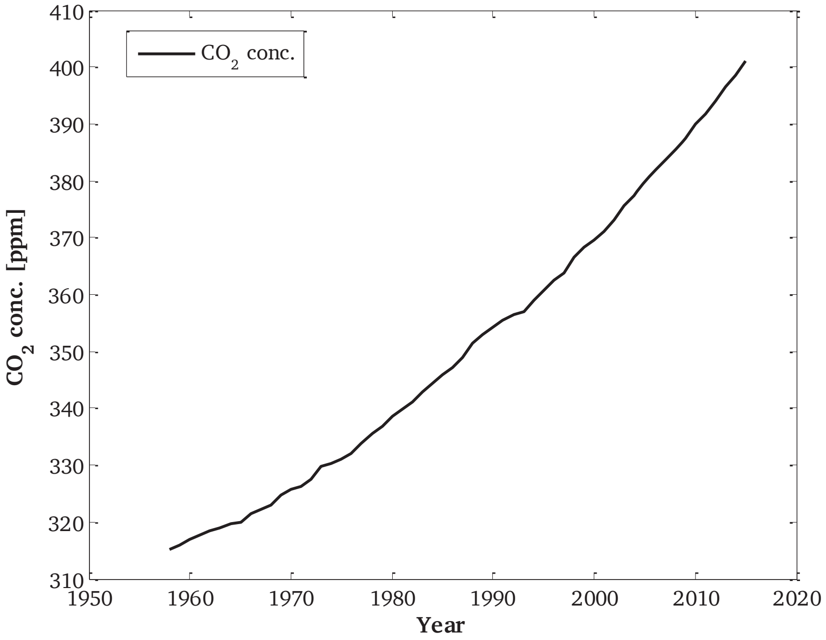

Figure 2: CO$_2$ concentration in the atmosphere over the last 65 years [11]

During the last years three scenarios describing the development of CO$_2$ emissions have been announced by the IEA. The Current Policy Scenario which does not assume any major changes in the government policies is consistent with the 6 °C scenario. It anticipates the energy use to nearly double until 2050 and the greenhouse gas emissions to even rise further. The average global temperature increase is expected to be about 6 °C in the long term. The second scenario called the New Policies Scenario takes into account global policy commitments by local governments to reduce greenhouse gas emissions. The latter is very similar to the 4 °C scenario requiring significant changes in technology and energy efficiency. The 450 Scenario is consistent with the goal of limiting the global temperature increase to 2 °C by limiting the emissions in the atmosphere to around 450 ppm. In this setting, the energy related emissions have to be reduced by more than half in 2050 compared to the year 2009.

The objective can only be achieved when the emissions from non-energy sectors are also reduced [12]. In the end of 2015, the 21st climate conference was held in Paris and the participating countries made more commitments to keep the rise in global average temperatures below 2 °C. All 196 nations have agreed to decrease the use of fossil fuels generating heat-trapping greenhouse gas emission as soon as possible without binding countries to specific carbon emission levels. These commitments were especially related to the energy sector, since this area accounts for more than two-thirds of the global greenhouse gas emissions. In anticipation of the conference in Paris new scenarios were defined by the IEA that differ from the ones described above. The INDC (Intended National Determined Contributions) scenario contains initial commitments and policy statements on the future energy trend. In this scenario renewables should become the leading source of electricity by

2030. The setting is consistent with an average temperature increase of around 2.6 °C by 2100 and of approximately 3.5 °C by 2200. The INDC scenario also includes commitments by major economies as China or India. In addition, it contains all recent or planned activities submitted to the UNFCCC in 14 May 2015 including Switzerland, European Union, Norway, Mexico, United States, Gabon, Russia, Lichtenstein and Andorra. These countries currently generate about 34 % of the energy related CO_2 emissions [9]. To remain below the 2 °C climate limit the IEA proposes a bridging strategy which could deliver a peak in energy related CO_2 emissions by 2020. The Bridge Scenario is based on proven technologies and policies without significantly changing the economic prospects of the countries. According to the World Energy Outlook Special Report [9] the Bridge Scenario depends on five major activities:

- Increasing the energy efficiency in industry, transport and building sectors
- Reducing the use of least-efficient coal fired power plants
- Increasing the investment in renewable energy technologies in the power sector from $270 billion in 2014 to $400 billion in 2030
- Phasing out of fossil fuel subsidies to end-users by 2030
- Reducing methane emissions in oil and gas production

The major reduction potential is estimated at nearly 50 % for the increase of energy efficiency, with about 26 % in the power sector alone. Reducing inefficient coal only counts to 9 %. Emissions in the Bridge Scenario would be 2.8 Gt (or 8 %) lower than in the INDC Scenario by 2025 and 4.8 Gt (or 13 %) lower by 2030. The CO_2 emissions have increased to 35 Gt in the year 2014. The long-term global temperature would rise above 2 °C even with the Bridge Scenario if no additional mitigation measures were taken later. The world would, however, need to be on track for further emissions reductions.

1.3 Carbon Capture and Storage

As mentioned in the previous chapter, CO_2 is responsible for more than 76 % of the anthropogenic greenhouse gas emissions. Especially the power generation sector is responsible for a large share of these emissions. CO_2 is obviously produced when fossil fuels are used for power generation or industrial processes. A technology named Carbon Capture and Storage/Utilization (CCS/U) can be applied in order to reduce the CO_2 emissions from these sources. There are three main categories for the capture process of CO_2.

Post-Combustion describes a technology which captures the CO_2 of the flue gases downstream the original combustion process. This technology is very simple and can easily be retrofitted to existing plants. By means of the Pre-Combustion technology, CO_2 is separated upstream the combustion process, whereas by the oxy-fuel technology, the fuel is burnt with pure oxygen instead of regular air thus producing a flue gas mainly consisting of CO_2 and water steam. All of these technologies need energy for capturing the CO_2 consequently lowering the overall efficiency of the process.

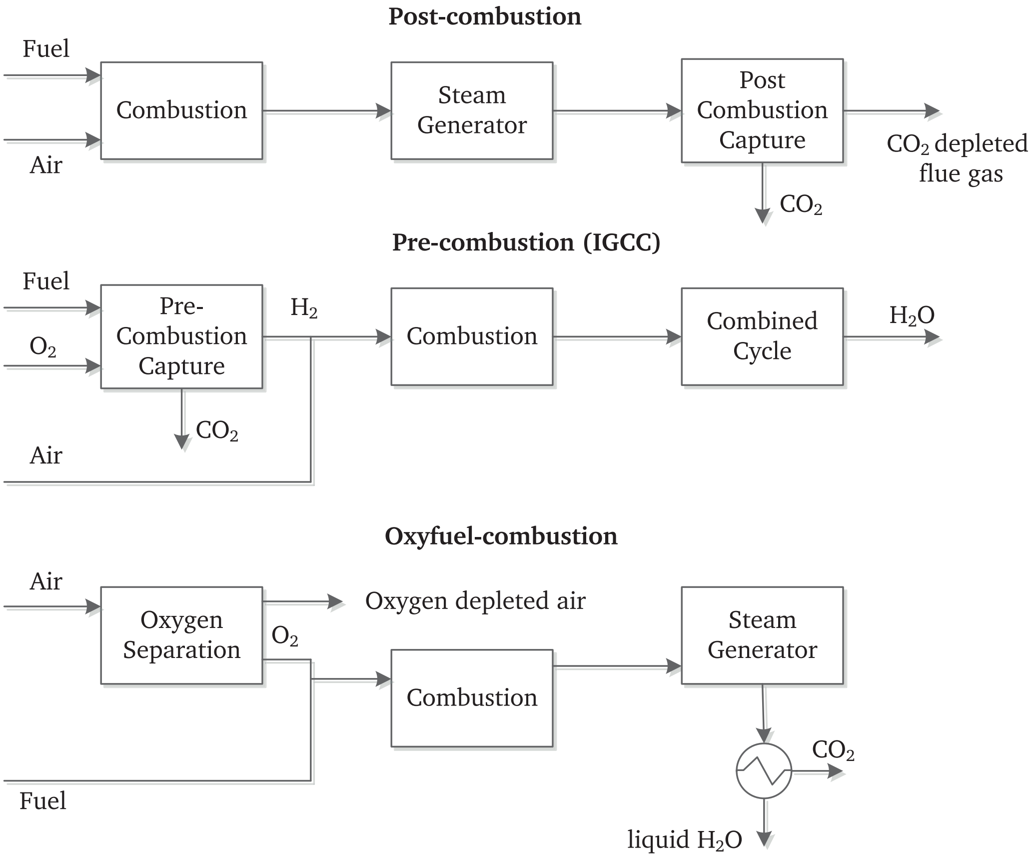

Figure 3: Overview of three main carbon capture process classes

Chapter 1.3 will mainly highlight the Pre-Combustion and the Oxy-fuel Technology, since the Post Combustion technology is described in detail in Chapter 2 as a core and fundamental basis of this thesis.

Pre-Combustion Technology

This technology refers to the removal of CO_2 from fossil fuels before the combustion is completed. This can be carried out in combination with an Integrated Gasification Combined Cycle (IGCC), where a gas and a steam plant are combined. A fuel is gasified with pure oxygen producing a synthetic gas mainly consisting of hydrogen (H_2) and carbon monoxide (CO). By means of a water gas shift reaction the CO is transformed to CO_2 and H_2. Due to a high partial pressure in the flue gas the CO_2 can now be captured through a physical or chemical absorption process.

The remaining H_2 is burnt in a gas turbine that is connected to a heat recovery steam generator. Nitrogen is mixed to the syngas to control the combustion temperatures. The advantage of this process is a high net electrical efficiency achieving 50 % without CCS [13]. With CO_2 capture, approximately 7 %-points efficiency reduction (compared to 50 %) can be expected [14]. The process also offers a wide variety in addition to the generation of electricity. Synthetic fuels or chemicals for example can be produced by means of the syngas.

Despite the high efficiency of the process high capital costs and a medium technological development of the hydrogen gas turbines need to be considered [15].

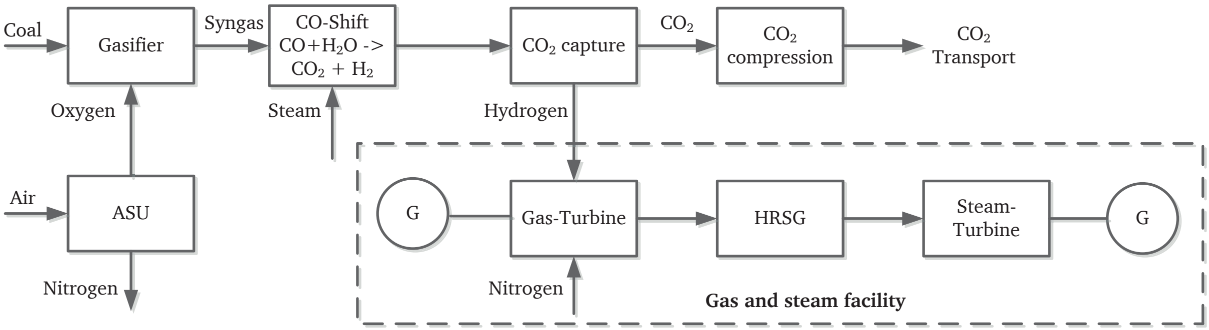

Figure 4: IGCC process with CO_2 capture

Oxy-fuel Technology

Oxy-fuel describes a combustion process in which the fuel is burnt in a nitrogen free atmosphere with pure oxygen. Since the combustion with pure oxygen leads to high temperatures in the furnace, flue gas is recirculated to control the temperature. The flue gas mainly consists of CO_2, water steam and a small amount of impurities as O_2 (due to false air), N_2 (due to remaining N_2 in the ASU), SO_2, NO_x and fly ash. The water steam can be condensed after the flue gas cleaning process and the relatively pure CO_2 stream can be further purified, compressed and transported/utilized. The simplified process scheme of this technology is depicted in Figure 5.

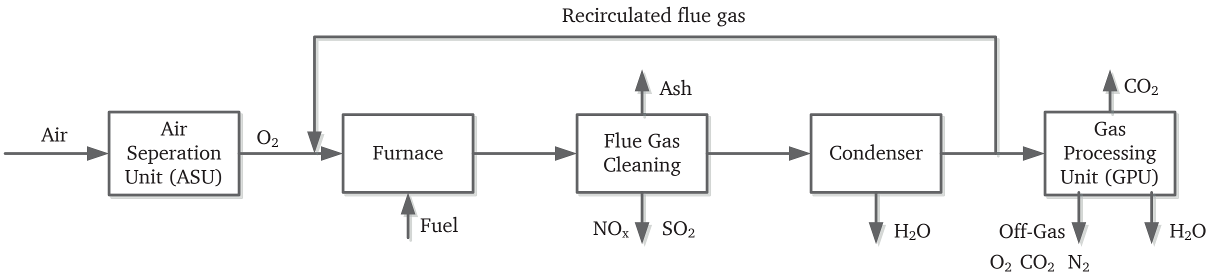

Figure 5: Simplified process scheme of the oxy-fuel technology

The firing with pure oxygen is very cost intensive, since oxygen has to be produced in an energy intensive air separation process. A common technology that is already available in large scale is the cryogenic Linde process separating air into its constituents by means of rectification. The pure gases are separated from the air by cooling the air until it liquefies, then selectively distilling the components at their various boiling temperatures. A second technology of the oxy-fuel group is the Chemical Looping process. Chemical-looping

Combustion (CLC) is one of the most promising carbon capture technologies [16]. It is characterized by a low energy penalty, low carbon dioxide capture costs and low environmental impact. To prevent the contact between fuel and air an oxygen carrier is used to transport the oxygen needed for fuel conversion. Figure 6 shows the simplified process setup.

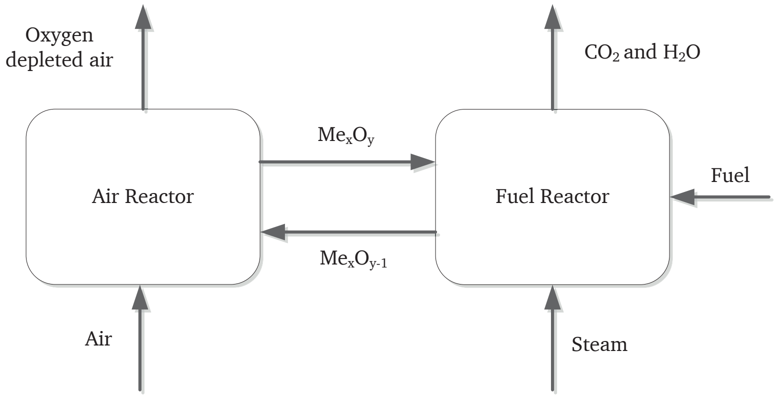

Figure 6: Chemical Looping process scheme

In comparison to a classic first generation oxy-fuel process, no air separation unit is required to provide the oxygen needed to burn the fuel. The solid fuel, such as hard coal, is gasified in the fuel reactor and the products from gasification are oxidized by the oxygen carrier. A very important step towards commercial application is the demonstration of the technology in auto-thermal operation, i.e. without electrically heated reactors. Hence, a 1 MW_{th} CLC pilot plant consisting of two inter-connected refractory-lined fluidized bed reactors was erected and successfully operated at Technische Universität Darmstadt [16, 17]. The first worldwide auto-thermal operation was achieved in several hundred hours of plant operation in the year 2014.

1.4 Research Objectives

The main scientific objective of this thesis is to achieve a technological proof-of-concept and an economical evaluation for the retrofit of an existing coal fired power plant and for a new plant with the indirectly heated and the standard carbonate looping process. Sufficient scale is needed to minimize wall effects and to enable auto-thermal operation of the system without electrical heating. A test unit with a thermal power of 1 MW_{th} can yield reliable information for full-scale plants and still implies reasonable investment and operating costs. A 1 MW_{th} pilot plant for the standard carbonate looping process was erected and operated at Technische Universität Darmstadt. This thesis describes some experimental investigations carried out in the Darmstadt plant. During the formulation of this work a new 300 kW_{th} pilot plant for CO_2 capture with the indirectly heated carbonate looping process was planned, erected and operated. The concept is based on a fluidized bed heat exchanger system transferring heat from a combustor to the calciner by means of heat pipes. The main advantage of an externally fired calciner is to avoid oxygen production by an air separation unit. The experimental